Effect of Sn and Ca Doping on the Corrosion of Pb Anodes in Lead Acid Batteries

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Introduction

Corrosion of positive grids in Lead acid cells will proceed continuously and shorten the lifetime of the battery. The rate of corrosion can be minimized by varying the float potential i.e. by polarizing the positive electrodes. The objective of the proposed study is to determine the corrosion rate of Pb-Sn (0.6%) and Pb-Sn(1.1%)-Ca(0.03%) alloys in 30% sulfuric acid solution under different applied potentials. The reversibility of these alloys under various potential scans has also been studied.

Experimental

Lead plates from NorthStar were cut into samples of 2" X 2" dimension. They were subsequently degreased with acetone and polished and washed with demineralized water. Two set of studies were done: (i) short range electrochemical studies and (ii) long range dissolution studies. A three-electrode setup was used to study the electrochemical behavior of Pb alloys. The electrolyte used in this study is 30% sulfuric acid with 10 g/L sodium sulfate. Lead grids of Pb-Sn (1.1%) were used as the counter electrode. Hg/Hg_2SO_4 was used as the reference electrode. All potentials in this study are referred with respect to the Hg/Hg_2SO_4 electrode. A PAR model 273A Potentiostat interfaced to a personal computer was used for data acquisition. Cyclic polarization, cyclic voltammetry and potentiostatic polarization studies were done on the different Sn alloys. Separately, seven samples each of Pb-Sn and Pb-Sn-Ca alloy were kept in 30% sulfuric acid solution for the long range dissolution studies. The samples were polarized to 1.2 V, 1.22 V, 1.25 V, 1.3 V and 1.35 V with respect to the Hg/Hg_2SO_4 electrode and the corrosion current was recorded as a function of time. After the test period of 3 weeks, the samples were removed, washed with DI water and the weight loss was determined. All studies were conducted at a temperature of 25^oC. The sample size for all studies was 8 $inch^2$ or 51.61 cm^2.

Results and Discussion

The reversibility of the Pb-Sn and Pb-Sn-Ca alloys can be studied using Cyclic Voltammetry. The alloy was cycled between 0.65V and 1.35V. Initially no peaks are seen in the forward scan (0.6V to 1.3V). Beyond 1.3 V a large increase in current is seen. This corresponds to formation of PbO_2 and oxygen evolution. On the reverse sweep, a large peak appears close to 1.07 V. This can be attributed to the conversion of PbO and PbO_2 on the surface to $PbSO_4$. After activating the sample for 5 cycles, CVs were continued at the same scan rate of 25 mV/s in the potential range of 0.6V-1.3V. In this case, a peak is seen in the forward scan also. This corresponds to the formation of PbO_2. In the first cycle the maximum in the oxidation peak is seen at 1.175 V. Subsequently this peak shifts slightly to more negative values and appears at 1.0 V. A characteristic feature of the CVs is the continuing increasing in the oxidation and reduction currents with cycling (Fig. 1). This indicates that more amount of Pb is converted to PbO_2 and $PbSO_4$ with cycling.

Similar behavior is seen for the Pb-Sn alloy also in the potential range 0.6V – 1.25V. In this case, the oxidation current at any given cycle is much smaller than that seen for the Pb-Sn-Ca alloy. This can be attributed to the lower Sn content in this alloy. However, beyond the first cycle, for both alloys the potential at which the peak oxidation and reduction current appears does not change. This indicates that a stable potential for $PbO_2/PbSO_4$ is established which does not change with cycling. Since, the goal of this study is to investigate the effect of polarization on corrosion characteristics it is essential to establish the reversible potential for PbO_2-$PbSO_4$ couple for both alloys.

The peak oxidation current increases with cycling for both alloys. However, the rate of increase decreases with cycling for the Pb-Sn-Ca alloy. For e.g. the peak current increases 48% for the Pb-Sn-Ca alloy between 100 and 300 cycles. However, between cycles 1500 and 1050 the increase is only 4.8%. However, a similar trend is not seen for the Pb-Sn alloy. For e.g. the peak current increases 7.55% between cycles 100 to 300 and 26.3% between cycles 1050 to 1500. Further studies need to be done to understand this difference in behavior between these alloys.

Acknowledgment

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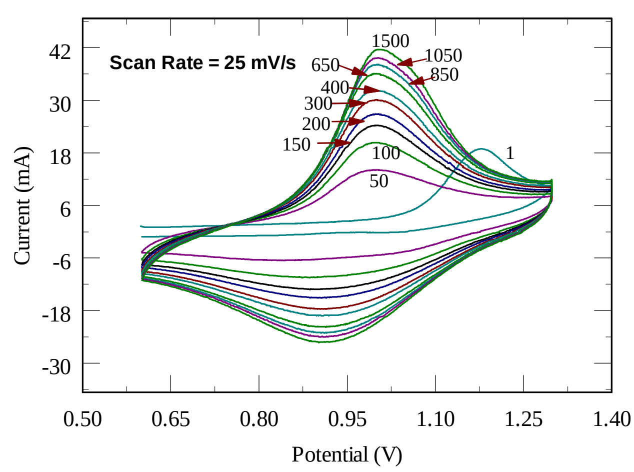

Figure 1. Cyclic voltammograms of the Pb-Sn-Ca alloy